Structural investigation of platinum solubility in silicate glasses

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ABSTRACT
The coordination environment of 20-200 ppm Pt in yellowish glasses from the CaO-Al2O3-SiO2 (CAS) ternary was studied using X-ray absorption fine structure spectroscopy at the Pt-LIII edge. Analysis of the Pt-LIII edge region suggests that Pt in these glasses is mainly tetravalent and sixfold-coordinated by O (with a mean Pt-O distance of 2.08 ± 0.02 Å). No evidence for Pt2+ or Pt6+ was found in any of the glasses studied, suggesting that one can not derive valence information easily from solubility data. No second-neighbor contribution was observed around Pt4+O6 polyhedra. However, bond-valence modeling suggest that these polyhedra are likely to bond mostly to [VI]Ca2+, which should promote high positional disorder of second-neighbor cations around Pt. This particular bonding arrangement may explain the relatively high solubility of Pt in these relatively depolymerized melts, as CaPtO3-type units.

INTRODUCTION
Platinum is a strategic element that is relatively insoluble in oxide glasses (usually less than a few parts per million). However, for some silicate melts containing large amounts of alkaline-earth elements, it is possible to dissolve larger amounts of Pt (i.e., >10 ppm). The Pt found in some synthetic silicate glasses is derived from corrosion of Pt-crucibles by the melt (Fairbairn and Schairer 1952; Ginther 1971; Higby et al. 1990) which imparts a yellowish color to glasses richest in Pt. For example, in low-silica calcium aluminosilicate glasses/melts prepared at one atmosphere pressure, enhanced Pt solubility can be observed (Dablé 1996; Azif et al. 1996; Amossé et al., unpublished manuscript) and may be as high as ~200 ppm as observed here (Table 1). Based on indirect solubility and electrochemical measurements, the enhanced solubility of Pt in CaO-Al2O3-SiO2 (CAS) melts under oxidizing conditions is related to the presence of oxidized valence states of Pt. Depending on the interpretation of experimental solubility data, Pt is thought to be in the +2 (Borisov et al. 1996) or +6 (Dablé 1996) valence state.

High Pt contents (above 100 ppm) are also observed in some oxide glasses used for nuclear waste storage (Kelm and Oser 1991; Pacaud et al. 1991). This Pt is generated by the decay of highly radioactive isotopes after storage for a few years. A better understanding of the structural factors that govern the enhanced solubility of Pt4+ in oxide glasses will help, for instance, to better extract this precious element from nuclear waste glasses.

To explore the structural origin of the enhanced solubility of Pt in CAS melts, we have undertaken an X-ray absorption fine structure (XAFS) spectroscopy study of Pt in various yellowish glasses from the CAS system containing trace amounts (as low as 20 ppm) of Pt. XAFS spectroscopy was used to determine the oxidation state of Pt in these glasses as well as its coordination environment. In addition, bond-valence considerations were used to derive plausible models of the medium-range structural environment around Pt in these glasses. Finally, structural information from this study was correlated with the solubility of Pt in these glasses/melts.

EXPERIMENTAL DETAILS
Glass synthesis
The nomenclature used to represent glass compositions here is Cax,y where x and y represent, respectively, the mol% SiO2 and Al2O3 components in the glass. The glasses were prepared by mixing reagent grade oxides SiO2, Al2O3, and CaCO3 in the desired amounts (Neuville 1992) (Fig. 1). The powders were slowly decarbonated at 1200 K and melted at 1900 K for 3-4 hours in a Pt crucible. The glasses were quenched from the melts by rapidly cooling the bottom of the crucible in water. The Pt present in the glasses derives directly from corrosion of the Pt-crucibles. In these glasses, the highest Pt contents were found in the most yellow glasses. Chemical analyses are in Table 1.

Pt-model compounds
Various model compounds representative of the coordination chemistry of Pt were investigated, including: metallic Pt, α-PtO2, Na3Pt(OH)6, K3PtCl6, and (NH4)2PtCl6 (Bandel et al. 1979; Siegel et al. 1969; Takazawa et al. 1984). Metallic Ptα

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TABLE 1. Chemical composition of the glasses studied (in wt%)

<table>
<thead>
<tr>
<th>Glass</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca₆₂₃</td>
<td>0.04(1)</td>
<td>53.13(1)</td>
<td>46.86(4)</td>
<td>195</td>
</tr>
<tr>
<td>Ca₈₉₂</td>
<td>8.93(3)</td>
<td>32.81(1)</td>
<td>55.87(7)</td>
<td>100</td>
</tr>
<tr>
<td>Ca₁₄₂₁</td>
<td>14.82(3)</td>
<td>31.20(8)</td>
<td>53.04(4)</td>
<td>&gt;20</td>
</tr>
<tr>
<td>Ca₁₀.₃₅</td>
<td>8.2(8)</td>
<td>49.9(6)</td>
<td>42.6(5)</td>
<td>&gt;50</td>
</tr>
</tbody>
</table>

Notes: Syntheses conducted in air and in platinum crucibles, run duration: 3–4 hours at 1900 K.
* Electron microprobe analyses done at the CAMPARIS, Paris. Data from Neuville (1992). Errors (2σ) are in parentheses.
† Values in ppm (ICP analyses done at CRPG, Nancy, France).

FIGURE 1. CaO-Al₂O₃-SiO₂ (CAS) ternary diagram showing the glass compositions studied.

represents the initial state of Pt⁰ prior to corrosion experiments. The four other reference compounds studied contain sixfold-coordinated Pt⁴⁺, with either O or Cl first neighbors around Pt. The average [⁴⁺]Pt-O and [⁴⁺]Pt-Cl distances are 2.00–2.06 Å and ~2.30 Å, respectively.

XAFS data collection

Data were collected at the Stanford Synchrotron Radiation Laboratory on wiggler beam line IV-1 at the Pt L₃-edge (11.56 keV). The storage ring operating conditions were 3 GeV of electron energy and 30–100 mA of electron current. A Si-220 double-crystal monochromator was used [energy resolution (FWHM) of ~3 eV at the Pt L₃-edge for a beam width of ~1 mm in the vertical direction; the Pt L₃-edge core hole width is ~5 eV]. Energy was calibrated using Pt metal foil. At all energies, the monochromator was detuned by 50% to eliminate higher energy harmonics in the incident X-ray beam. The incident- and transmitted-beam intensities were monitored with an ionization chamber, using Ar as the absorbing gas. Because self-absorption is unlikely to be a problem for Pt at these relatively low concentrations, absorbance was measured by monitoring fluorescence yield as a function of X-ray energy using a Stern-Heald-type detector with Ar in the fluorescence detector ion chamber. A Ga₂O₃ filter (9 µm absorbance) was used to minimize unwanted fluorescence and scattered radiation. Because of the low Pt contents in the glass samples, XAFS spectra were obtained by averaging four to ten individual scans for each sample to improve the signal-to-noise ratio.

XAFS data analysis

Extended X-ray absorption fine structure (EXAFS) spectra were normalized in absorbance using a Victoreen and a spline function (with 10 external double knots, Winterer 1996). Energies were recalculated into k space (where k is the momentum of the photoelectron) with “E₀” (i.e., the energy where k is zero), arbitrarily chosen at the half-height of the absorption step (modeled with an arc tangent function). The k⁻²-weighted EXAFS spectra were Fourier transformed (FT: Kaiser-Bessel type) over the k range 2 to 10 Å⁻¹. The resulting modulus of the FT is a curve similar to a radial distribution function (RDF). However, the FT contains pair correlations involving only the central absorber (in this case Pt) and surrounding atoms and it is uncorrected for the phase-shifts of photoelectron waves as they interact with various surrounding atoms. The last step of data analysis consists of backtransforming the real and imaginary parts of the RDF (1–2.2 Å range). Modeling of these FT-filtered EXAFS oscillations using anharmonic and curved-wave theories (Crozier et al. 1988; Rehr et al. 1986) gives average structural parameters for the Pt environment: identity of first-neighbor atoms, average distance between Pt and these neighbors (R), average number of first neighbors (N), a Debye-Waller-type factor (σ²), and an anharmonic parameter (Cᵢ). The last two parameters provide a measure of relative disorder and anharmonicity of the Pt-O pair-correlation probed. Backscattering O amplitude and Pt-O phase-shift functions were calculated using the FEFF7 code (Zabinsky et al. 1995). Modeling of the normalized, raw EXAFS spectra could not be performed because of the presence of a multiple-scattering (MS) feature in the low-energy region of the spectra (particularly near 11590 eV on Fig. 2), as will be demonstrated by X-ray absorption near edge structure (XANES) calculations (see below). This MS contribution adds a relatively intense peak in the FT (half that for Pt-O) near 2.5 Å. It arises from multiple paths of the photo-electron inside the PtO₄ units involving the central Pt atom and two oxygen first neighbors (MS path of order 3).

RESULTS

Solubility of Pt is highest for glasses with Ca-rich compositions in the CaO-Al₂O₃-SiO₂ ternary (Table 1). Also, the presence of alumina in the melt increases the dissolution of Pt, in contrast to silica. Only glasses Ca₈₀₃₉, Ca₁₀.₂₂₁, Ca₁₀.₃₅₂, and Ca₁₆.₂₁ could be studied by XAFS spectroscopy because they were the most enriched in Pt (20–200 ppm Pt). However, it should be possible to carry out XAFS studies of glasses with even lower Pt concentrations in the near future because of the availability of higher X-ray fluxes on third generation synchrotron radiation sources.

XANES spectroscopy

The XANES spectrum for Pt⁴⁺ model compounds (Fig. 2, left) is characterized by a sharp, intense Pt L₃-absorption edge. This absorption edge is caused by the excitation of an electron
from the 2p\textsubscript{3/2} core level to empty valence and continuum levels (see Horsley et al. 1982; Mansour et al. 1984). The intensity of the absorption edge has been directly related to the density of unoccupied d states (allowed transition from 2p to 5d levels). However, others attribute these features to multiple-scattering effects of the ejected photoelectron wave from the central absorbing atom among its nearest and next-nearest neighbors (e.g., Natoli and Benfatto 1986). In using the FEFF7 multiple-scattering formalism to model the Pt L \textsc{iii} edge region, we have verified the appropriateness of the latter interpretation. The characteristics and origins for these edge features are presented below.

The Pt L \textsc{iii}-edge crest

The absorption edge is more intense for the Pt\textsuperscript{iv} model compounds considered than for metallic Pt. Also, the energy position of the absorption edge feature is shifted toward higher energies with increasing Pt-oxidation state by ~2 eV (Fig. 2, left). There is also a weaker but significant variation in the absorption edge position and intensity as a function of the Pt-redox state and nature of the ligands (O vs. Cl), as measured experimentally (e.g., left).

Also, the energy position of the absorption edge feature is shifted toward lower energy values when compared to Pt-oxide model compounds (10–12 eV shift). Based on ab-initio XANES calculations, we are able to assign this feature to MS effects within the coordination sphere of Pt\textsuperscript{iv}, as explained below.

Ab-initio XANES calculations

These calculations (using the FEFF7 code, Rehr et al. 1992; Zabinsky et al. 1995) were undertaken for typical PtO\textsubscript{6} and PtCl\textsubscript{6} clusters (seven atoms) to ascertain the previous qualitative assignments of the XANES features (Fig. 2, right). The cluster structure information is taken from the model compounds Na\textsubscript{2}Pt(OH)\textsubscript{6} and K\textsubscript{2}PtCl\textsubscript{6}. The FEFF7 code can be utilized to calculate XANES spectra for single-scattering events (such as that related to a Pt ↔ O path of the excited photoelectron which corresponds to a single O backscatterer) as well as for multiple-scattering events (e.g., O ↔ Pt ↔ O, involving several O backscatterers). MS paths up to 6 Å in length were included in the XANES calculations for these simple PtO\textsubscript{6} or PtCl\textsubscript{6} clusters. Self-consistent Hedin-Lundqvist potentials were used (see Zabinsky et al. 1995), and the energy of the Fermi level was corrected by +4 eV to account for the +4 oxidation state of Pt. All spectra were shifted by +25 eV to correspond with the experimental monochromator energy calibration. All other FEFF7 parameters were set to their default values. For each cluster (PtO\textsubscript{6} and PtCl\textsubscript{6}), the XANES spectra were calculated assuming two models: first, single-scattering (SS) contributions only, and, second, the sum of single- and multiple-scattering contributions (Fig. 2, right).

Comparison of the ab-initio XANES spectra with the experimental spectra confirms that the experimental Pt L \textsc{iii}-edge data can be accurately reproduced assuming SS and MS effects involving only the first shell of neighboring atoms around the central Pt. The MS feature located at ~10–20 eV above the absorption edge is observed only when MS paths are included in the calculation. Ab-initio calculations also suggest that this MS feature is affected in position and intensity by the nature of the ligands around Pt\textsuperscript{iv}. For Cl-first neighbors, its position is shifted to lower energies compared to that observed for Pt-O ligands (it is also less intense). In the FEFF7 calculation, this feature results from a O ↔ Pt ↔ O scattering path of the ejected photoelectron within the PtO\textsubscript{6} cluster. This path has an effective length R of about 3.7 Å. For the PtCl\textsubscript{6} cluster, the same type of MS contribution is detected but with a greater length (R = 4.0 Å), because of the larger ionic radius of Cl compared to O (~1.7 and 1.4 Å, respectively). Because the energy position of XANES features is correlated with R \textsuperscript{2} (see Natoli and Benfatto 1986, among others), the MS feature for the PtCl\textsubscript{6} cluster should therefore be located at a lower energy compared to that for PtO\textsubscript{6}, which is what we observe.

XANES for the Pt-glasses

For the Pt-glasses studied (Fig. 3), the Pt L \textsc{iii}-XANES spectra are similar to those observed for Pt\textsuperscript{iv}–O model compounds [\(\alpha\)-PtO\textsubscript{3}, Na\textsubscript{2}Pt(OH)\textsubscript{6}]; the Pt L \textsc{iii}-absorption edge is intense and centered around 11569.5 eV. This suggests that Pt is mainly
tetravalent in the glasses studied. No significant amounts of metallic Pt or any other reduced or highly oxidized Pt-species (such as Pt\(^\text{0}\), Pt\(^{+}\), or Pt\(^{6+}\)) were detected (indicating they are absent or present at concentrations less than 10 at\%). In addition, the MS feature located at \(~20\) eV above the absorption edge is observed, like in the NaPt(OH)\(\text{6}\) and \(\alpha\)-PtO\(\text{2}\) model compounds (Fig. 3).

**EXAFS spectroscopy**

The FT values for the model compounds (Fig. 4) show an intense contribution centered around \(~1.7\) Å [as in NaPt(OH)\(\text{6}\) and \(\alpha\)-PtO\(\text{2}\)]. \(~2\) Å [K\(_2\)PtCl\(\text{6}\) and (NH\(_4\))\(_2\)PtCl\(\text{6}\)] and \(~3\) Å (metallic Pt). In the FT values, distances are uncorrected for backscattering phase-shifts. This contribution is due to the presence of first neighbors around Pt (O, Cl, or Pt, respectively). The larger ionic radius of Cl compared to O causes the Pt-Cl peak to shift to longer distances compared to Pt-O pairs. These model compounds show little evidence for next-nearest neighbors around Pt because of disorder effects (positional and thermal, see Brown et al. 1995).

The absence of Pt-Pt contributions near \(~3\) Å in the FT for the Ca\(_{0.39}\) and Ca\(_{10.23}\) glasses (Fig. 5, left) rules out the presence of significant amounts (<10\% of the total Pt atoms) for metallic Pt in these samples. This result is in agreement with the XANES results (presence of an intense absorption edge shifted toward higher energy). In contrast, the FT values calculated from the EXAFS spectra of the glasses (Fig. 5, right) show an intense peak centered around \(1.7\) Å (uncorrected for backscattering phase-shift). This contribution arises from O atoms first neighbors around Pt, like in the NaPt(OH)\(\text{6}\) model compound. Fitting of EXAFS oscillations for the Ca\(_{0.39}\) and Ca\(_{10.35}\) glasses gives \(6.6\ \pm\ 1\) oxygen atoms around Pt at an average Pt-O distance of \(2.08\ \pm\ 0.02\) Å (Table 2). The PtO\(_6\) polyhedra show relatively little radial distortion (the anharmonic C\(_3\) parameters are nearly zero). The EXAFS-derived average Pt-O distance for the glasses studied is consistent with that observed for Pt\(^{4+}\)O\(_6\) polyhedra in crystalline NaPt(OH)\(\text{6}\) (Bandel et al. 1979). Some minor or trace amounts of other Pt-coordinations (4 and/or 5, if possible) are not excluded in these glasses, but sixfold coordinated Pt\(^{4+}\) is the dominant species.
The peak near 2.5 Å in the FT arises from MS effects within the PtO$_6$ units (this peak disappears from the FT when the FT is calculated for a $k$-range starting above $k = 4$ Å$^{-1}$). No clear evidence for second-neighbor contributions (Pt, Al, Si, or Ca) around the PtO$_6$ polyhedra was detected in either glass. EXAFS spectra for the two other glasses (Ca$_{0.23}$ and Ca$_{0.21}$) were not collected because the signal-to-noise ratio is too low and because their XANES spectra are similar to those collected for the two other glasses investigated in this study (Ca$_{0.39}$ and Ca$_{10.35}$).

**DISCUSSION**

The structural and oxidation state information derived from XANES spectra of the Pt-containing glasses in the CaO-Al$_2$O$_3$-SiO$_2$ ternary is consistent with that derived from the EXAFS spectra and suggests the presence of Pt$^6$O$_6$ polyhedra. No significant amounts (<10 at%) of Pt$^0$ and/or Pt$^{2+}$ were found in these glasses. Thus, the solubility of Pt is clearly favored under oxidizing conditions in the Pt$^{4+}$ form, which is similar to the correlation between solubility and oxidation state observed for other cations with variable oxidation states (e.g., Mo, U, Veal et al. 1987). These results are consistent in part with the electrochemical information derived for Pt in similar glasses (Dablé et al. 1996), whereas Pt$^{4+}$ is found to be a major Pt-species in CAS melts prepared under moderately oxidizing conditions. These experiments also suggest the presence of large amounts of Pt$^{4+}$ in the most calcic glasses of this ternary system synthesized under oxidizing conditions. However, our direct XAFS results do not confirm this suggestion. Also, no evidence for Pt$^{2+}$ was found in any of the glasses studied, as previously suggested from solubility experiments (Borisov et al. 1996). Our direct spectroscopic results therefore suggest that the interpretation of solubility information for Pt as a function of the oxygen fugacity is not straightforward. A slope of $\pm 1/2$ in the plot of the Pt-concentration in glasses as a function of oxygen fugacity during synthesis may not always be indicative of Pt$^{4+}$. Other factors, such as the formation of a passivation layer around Pt particles, may influence the slope in these plots (Amossé et al. 1990; Dablé et al. 1996; see also Capobianco et al. 1994).

**Medium-range environment of Pt$^{4+}$**

Unfortunately, no information can be derived from XAFS about the medium-range structure of Pt$^{4+}$ in these glasses because there is no clear contribution in the FT above 3 Å. The lack of second-neighbor information in the XAFS spectra of Pt in these glasses is in contrast to the XAFS spectra of other cations such as Zr$^{4+}$ and Ti$^{4+}$ in similar glasses which show clear second-neighbor contributions in their FT values (Farges et al. 1991; Farges 1999). This lack of information may be due to a complex medium-range structural environment around Pt$^{4+}$ in the CAS glasses being considered. Data collection near 4 K in these glasses can be performed to minimize the effects of thermal disorder on XAFS spectra (and therefore can promote contributions from second neighbors such as weakly bonded network modifiers which should exhibit significant thermal motion even at room temperature). However, it was not technically feasible to collect low temperature XAFS data with the currently available XAFS spectrometers and sample cryostats, given the very low Pt concentrations in these CAS glasses. Also, most of the available XAFS data for highly charged cations in silicate glasses show that collecting data at very low temperatures does not result in a dramatic improvement in EXAFS spectra (i.e., there is little improvement in resolution of second-neighbor frequencies). This observation suggests that the lack of second-neighbor contributions in the Pt L$_{III}$-EXAFS.

**TABLE 2.** EXAFS-derived anharmonic structural parameters for the glasses studied.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Oxygen shell</th>
<th>$N$</th>
<th>$R$ (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$C_3$ (Å$^3$)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$_{0.39}$</td>
<td>6.6</td>
<td>2.09</td>
<td>0.009</td>
<td>0.00020</td>
<td>0.057</td>
<td></td>
</tr>
<tr>
<td>Ca$_{0.21}$</td>
<td>6.7</td>
<td>2.08</td>
<td>0.011</td>
<td>0.0015</td>
<td>0.063</td>
<td></td>
</tr>
<tr>
<td>Error (%)</td>
<td>1</td>
<td>0.02</td>
<td>0.002</td>
<td>0.0005</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Chi-square factor of the fit to the data.

Notes: $N, R, \sigma^2$, and $C_3$ are, respectively, the number of neighbors, the average Pt-O distance, the absolute Debye-Waller-type factor, and the third-order anharmonic cumulant at 293 K.
spectra of the CAS glasses is more likely related to a high degree of positional disorder in the medium-range environment around Pt.

The lack of discernible second neighbors around Pt in the CAS glasses may therefore be related to a preferential connection of the PtO₆ units to network modifiers (Ca) instead of network formers (Si, Al). Also, Pt⁺⁺⁺ is found mostly in oxide compounds, with very few Pt-silicates known. The FT of Na₄Pt(OH)₆ (Fig. 4) is a good example of the presence of weakly bound second-neighbor cations around Pt on the Pt L₃-edge EXAFS spectrum; in this compound, Na second neighbors could not be detected because of their significant thermal and positional disorder around Pt.

**Bond-valence models**

To test the hypothesis that Pt in the CAS glasses has Ca second neighbors we can use a bond-valence model to examine different types of second-neighbor environments around the PtO₆ polyhedron. This model (see Farges et al. 1991) is based on the idea that Pauling’s second rule (Pauling 1929) should be valid for oxide glasses. The Pt-O bond provides ~0.7 valence units (v.u.) (~6 ~0.7 v.u.). To calculate Ca-O, Al-O, and Si-O bond valences, we must know the coordination numbers of Ca, Al, and Si cations in such glasses (reviews of such data can be found in Brown et al. 1995 and Stebbins 1995). These reviews suggest that Si and Ca are mostly likely fourfold and sixfold coordinated, respectively. The bond valences for [IV]Si-O and [IV]Ca-O bonds are around 1.0 and 0.3 ± 0.05 v.u., respectively. For Al-O bonds, the bond valence is about 0.75 because the main Al-coordination in these glasses is fourfold (Engelhardt et al. 1985; Poe et al. 1994; Stebbins 1995) in agreement with thermodynamic and Raman scattering information (Neuville et al. 1994). Higher Al-coordinations (five or six) have been reported in these glasses (Poe et al. 1994; Giuli et al. 1995) but at minor levels (no more than ~20% of the total Al). However, in the medium-range environment around Pt these higher Al-coordinations cannot be excluded because [IV]Al/[VI]Al, if present, could be more abundant than Pt⁺⁺⁺ in these glasses.

Based on the assumptions stated above, the bond-valence model can be used to derive two plausible structural arrangements around O atoms of a PtO₆ polyhedron (Fig. 6). One possible structural arrangement involves one Pt, one Ca, and one Si bonded to O (see O₁ atoms in Fig. 6). The valence balance around O₁ atoms (0.7 + 0.3 + 1.0 = 2.0 v.u.) satisfies Pauling’s electrostatic valence principle at room temperature. The O₁ atoms are threefold-coordinated and non-bridging (NBO), and the presence of some Si is required in the glasses in order to achieve valence balance. When Al replaces Si (see O₂ atoms in Fig. 6), two Ca atoms are required around oxygen to compensate for the deficit of bond valence due to this substitution (0.7 + 2 × 0.3 + 0.75 = 2.0 v.u.). O₂ atoms are fourfold coordinated NBOs and require [IV]Al for valence balance. Other plausible bond-valence models can be postulated with [IV]Al or [VI]Al in the second-neighbor coordination shell of Pt⁺⁺⁺ if we assume that these Al coordinations are present at significant levels in these CAS glasses. For example, fourfold coordinated NBOs are possible bonded to two Ca and one [IV]Al or bonded to one Ca and two [VI]Al (O, and O₅ atoms, respectively, in Fig. 6).

![Figure 6. Bond-valence model of the local structure around Pt⁺⁺⁺ in the oxides studied. Pt⁺⁺⁺ must bond to non-bridging O atoms which may be threefold or fourfold coordinated, respectively: [IV]O₂ atoms are surrounded by one [IV]Ca and one [III]Si (less likely because Pt solubility is not high in melts with Si-rich compositions); [IV]O₂ atoms have two [VI]Ca and one [IV]Al nearest neighbors. Two other types of O atoms bonded to [IV]Al and/or [VI]Al (O₅-type and O₆-type) are also plausible. Finally O₅-type atoms, bonded only to [IV]Ca, may be the most common type of NBO around Pt⁺⁺⁺ in CAS glasses.](image)

Finally, a model with only network modifiers (Ca) bonded to the O atoms coordinating Pt (through O₂ atoms) is also possible. This type of second-neighbor environment around Pt is found in the model compound Na₄Pt(OH)₆. Medium-range structural environments around Pt that are combinations of the models presented here are also possible.

**A structural model for the solubility of Pt⁺⁺⁺ in oxide glasses**

The presence of O₅-type O atoms around Pt is less likely because Pt-contents in the CAS glasses increase with decreasing SiO₂ contents, suggesting little structural correlation between Pt and Si in these systems, as previously stated. Corner sharing of PtO₆ octahedra and AlO₄ tetrahedra may be a more likely type of linkage (models involving O₅-type O atoms) because [IV]Al is by far the most abundant Al-species in glasses/melts of this ternary system (alternative models involving [IV]Al and [VI]Al are also possible through O₅- and O₆-type O atoms). O₂-type O atoms around [V]Pt⁺⁺⁺ would require ~6 Al and 12 Ca in the medium-range environment of Pt. This large number of weakly bonded Ca atoms, which can have a relatively wide range of Ca-O distances and Ca-O-Pt angles, should result in a disordered medium-range structural environment around Pt. This suggestion is consistent with the lack of detectable sec-
ond neighbors in the Pt $L_{III}$ edge EXAFS for these glasses. The same conclusions can be reached for $O_{2}$-type O atoms. Therefore, previous qualitative models of the medium-range environment of Pt, which suggest “CaPtO$_n$” units based on solubility and electrochemical measurements (Antonenkova et al. 1989; Dablé 1996), are consistent with the bond-valence models shown in Figure 6.

In conclusion, the solubility of Pt$^{+}$ in CaO-Al$_2$O$_3$-SiO$_2$ glasses/melts examined in this study is consistent with the presence of a large number of network modifiers, such as Ca, around Pt. Also, some oxygen dissolved in the melt (in equilibrium with the atmosphere of the furnace) is required to favor the oxidation of metallic Pt (Dablé 1996). Network modifiers (Me) with similar Me-O bond valences (~0.3), as well as relatively small alkali cations (such as Na), should also promote Pt-solubility. If we assume that CAS glasses and melts contain two types of percolation domains (one consisting primarily of the network formers Si and Al, and one consisting primarily of the network modifier Ca (Eckersley et al. 1988; Gaskell et al. 1992) then Pt$^{+}$ should be strongly partitioned into the Ca-rich domains, as CaPtO$_n$-type units.

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